Journal of Advances in Science and Technology
Vol. 19, Issue No. 2, April-2022, ISSN 2230-9659

A Study the Experimental Method of Preparation of Tin Oxide Thin Films

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Abstract- Gas sensors are used in environmental observing, industrial safety, disease diagnostics, & traffic safety. Toxic environmental pollutants & dangerous gas escapes from factories are two of their most common uses. gas sensors use a physical change, which in turn generates an electrical signal whose amplitude is directly proportionate to the gas concentration. There are various experimental techniques available to prepare metal oxide thin films and these are studied by different characterization techniques to understand their physical and chemical properties. In this paper, a detailed account of the method of preparation of Tin Oxide thin films has been discussed. This includes method of preparation of precursor solution, surfactants used etc., and a detailed description of the Chemical Spray Pyrolysis unit, which is used for the deposition of Metal Oxide thin films in the present work.

Keywords- Gas Sensors, Thin Films, Metal Oxide, EDAX SEM

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INTRODUCTION

The physical & chemical properties of metal oxide thin films can be understood through the adoption of several characterisation approaches, which can be achieved through a variety of experimental methods. A comprehensive description of the process for making thin films of tin oxide has been covered in this chapter. In this study, metal oxide thin films are deposited using a Chemical Spray Pyrolysis unit, which is described in detail. The technique of synthesis of the precursor solution, surfactants utilised, etc. are also included. The benefits of CSP compared to alternative deposition methods have been emphasised. Several characterisation methods have been employed to comprehend the chemical and physical characteristics of thin films. Various devices used to characterise the deposited films are described briefly along with their functioning principles. Methods such as electrical characterisation, scanning electron microscopy, energy dispersive X-ray diffraction (EDAX), ultraviolet-visible spectroscopy, & X-ray diffraction (XRD) are all part of this category.

LITERATURE REVIEW

G. Fang et al. (2010), stated CeO2- SnO2 thin films for sensing gas at room temperature have report sensing properties S.Dhage et al., identified nanocrystalline powder synthesis C.V Gopal Reddy et al. (2013), proposed vapor ethanol detection with TiO2 and WO3 sensors, S.Dhage et al. J. Wang etc., the BaTiO3 moisture sensor recorded and the result of doping studied. C. Baratto et al, have synthesized SnO2 nano wires for gas sensor investigations utilizing vapor phase deposition. P.G. Su et al., recorded nitrogen dioxide detection with a thick film semi-conductor sensor centered on mixed tungsten oxide. For the improved H2S sensor, S.V. Manorama et al. have synthesized SnO2 nano particles using the sol-gel method. The stability & oxidation of the sandwich form gas sensor on thin films were recorded by Kaldikas et al. In2O3 & MoO3-In2O3 thin films have been used by A. Gurl et al., NO2 and O3.

K.S. Yoo et al. (2015), The thin nano-grained Indium tin oxide films for sensing H2 have been created. As an H2S sensor, Ag doped SnO2 thin film was investigated by C.H. Liu et al. The impact of additives on gas sensing & structural properties of In2O3-based ceramics has been identified by G. Korotcenkov et al. The In2O3 SnO2 composite thin NO2 sensor films have also been synthesized by Roreleo et al. A. J. P. Ahna et al. developed thick films for the microstructure using SnO2 nanophase and analyzed the gas sensors. E. Zampicenia et al. identified an effect on composition of the characteristics of sputtered SnW-O films. Gouma built thin conductometric sensors based on MoO3 and WO3 for automotive applications on thin, film-based films. In sol-gel dependent thin films, K. Oomman et al. registered strong ethanol sensitivity. E. Comini et al., have nanobelts made out of Tin oxide and have their electrical and sensory characteristics tested. A. Ponzani et al. have documented the deposits of nanostructured WO3 for gas sensing applications by adjusted thermal evaporation. The proof of bending flattening in SnO2

polytrystalline 10nm has been demonstrated by C. Malagu et al. M. Kroneld et al. studyed SnO2 thin film gas sensing characteristics generated using MBE methodology.

A.M. Nortowski (2013) Recorded sol-gel synthesis of sub-micron titanium-doped gas sensing chromium powders. C. Garzellaa et al., utilizing sol-gel spin coating W/TiO2, have produced a new selective ethanol sensor. A.K. Prasada et al. contrasted the MoO3 thin movie gas sensors for selective ammonia detection deposited with the sol gel and ion beam. G. Neri et al. have nano powders for low-temperature oxygen sensors synthesizing In2O3 and Pt-In2O3. The characteristics of cobalt-doped SNO2 thin movies were recorded by Shriram B. Patil et al. N.G. Patel et al. recorded thin film gas sensor Indium tin oxide (ITO) at room temperature for methanol detection.

V. Guidi et al. (2014), Synthesized tungsten trioxide powders for the detection of NO2 by aqueous and alcoholic routine. The effect of iron addition on ethanol & CO sensing properties of the tin ready with the RGTO technique has been studied by E. Comini et al. The surface adjusted BaTiO3 thick film resistors as H2S gas sensors were examined by G.H. Jain et al. The thin film indium oxide by spin coating process was prepared by W.Y. Chung et al. and its gas sensing properties were investigated. The effect and additive effect of thermal treatment have been studied by V.V. Kovalenlo et al., surface chemistry for nanocrystalline SnO2. M. Kaur etal. have identified the development and implementation for room temperature sensing of Zn/ZnOnanostructures through thermal evaporation. The structural characterization of nanocrystalline SnO2 powders was prepared by and carried out by M.J. Zheng et al. B.R. Mehta and V.N. Singh stated In2O3 — Ag composite nanoparticle layers for structural, electrical and gas sensing properties.

A. Zannia et al. (2015), Reported a novel gas sensing material, Vanadium and tantalum-doped titanium oxide. The synthesis & characterization of semiconducting nana cables for gas sensing is proposed by G. Sberveglieri et al. P. Bhattacharyya et al. registered noble metal catalytic contacts with thin methane sensing sol-gel zinc oxide. The impact of Fe doping on the gas sensing properties of nanocrystalline thin films SnO2 has been examined by S. Rani and others. Neri et al. have announced improved gas sensing performance: SnO2-based nanocrystalline oxides. In_2O_3–doped SnO_2 thick film sensors registered CO properties: effect of doping concentration and size of grain.

Fu et al. (2011) Using a chemical bath deposition technique, they obtained standardized hierarchical ZNO nanostructures. Xu et al. used liquid-phases chemical procedure to synthesize ZnO nanowires. The Nanoscale Porous ZnO Structure, consisting of flake-form particles synthesized using CBD procedure, is synthesized by Abdullah et al. [52]. The pore ZnO films deposited on the FTO-coated glass substrates with sol-gel process have been synthesized by Hossain et al. Zhang et al. published a process of synthesizing the hierarchical ZnO nanostructure on ITO glass in a neutral solution in two stages. Zhang et al. obtained wet-chemical nanosphere ZnO hierarchically ordered. Gao and others used the low temperature CBD process to synthesize ZnO nanorod thin films. ZnO porous and spherical nanostructure was synthesized by Yadav et al, with the hydrothermal approach. Hou et al. are the two-stage hydrothermal system used to produce ZnO microrods. Qiu et al. are using a hydrothermal approach to preheat ZnO nanorod arrays synthesized with a diameter of 70 nm and duration of 10 μm. Zhu et al. [60] synthesized ZnO nanorods without adding surfactants or complexing agents by using hydrothermal process. Using the hydrothermal process, Urchin-like arrays consisting of ZnO nanorod needle-type nanorods of 40 nm diameter. Cobalt doped Zink Oxide Zn 1−xCoxO nanorods (x = 0,01, 0,10) have been synthesized by loans et al. using a hydrothermal process. Ma et al. have ZnO nanorod arrays synthesized through the hydrothermal approach.

MATERIAL AND METHODS

The SnO2 thin films were synthesised using only ingredients of analytical grade, which do not require further purification. The precursor, stannous chloride (SnCl4.5H2O), was sourced from Thomas Beker in India. Himedia Laboratories Pvt. Ltd. of Mumbai is the source for TX-100 [C14H22O(C2H4O)n]. Fisher Scientific India Pvt. Ltd. of Mumbai is where PEG6000 is purchased. Synthesis of SnO2 films is accomplished using our in-house chemical spray pyrolysis apparatus. The substrates utilised were commercially available laboratory glass slides with dimensions of 25 mm x 75 mm & thickness of 1 mm. As a probing gas, H2S was employed.

PREPARATION OF PEG SOLUTION

All of the synthesis was carried out using ethanol (C2H5OH), which was procured from sdfine chemicals in India. Sodium stannous chloride (SnCl4.5H2O) was dissolved in ethanol, then subjected to brief sonication in an ultrasonic bath, and finally filtered through filter paper to produce a transparent precursor solution for the deposition of SnO2 thin films. The solution's concentration is kept at 0.2M. To generate the solution for deposition of SnO2-TX100 composite thin films, 20 ml of SnCl4 precursor solution was mixed with T X-100 in increments of 1% (0.2 ml), 2% (0.4 ml), 3% (0.6 ml), 4% (0.8 ml), 5% (1 ml), and 6% (1.2 ml). The mixture was then sonicated for two to three minutes to ensure homogeneity. Thin films of SnO2-TX100 composite were deposited using the solutions that had been produced.

Composite thin films made of SnO2 and PEG6000 have been deposited. To achieve a clear solution with a concentration of 0.01M, PEG6000 was

dissolved in ethanol and subjected to sonication for approximately 20 minutes. To make it homogeneous, 20 ml of the already-made precursor solution of SnCl4 was sonicated for 2-3 minutes after adding the prepared PEG solution in increments of 1% (0.2 ml), 2% (0.4 ml), 3% (0.6 ml), 4% (0.8 ml), 5% (1 ml), and 6% (1.2 ml). The SnO2-PEG 600 composite thin films were deposited using these solutions.

PREPARATION OF SNO2 THIN FILMS

Thin film deposition is accomplished using our home-made Chemical Spray Pyrolysis apparatus. The prepared solutions of SnCl4, SnCl4 with TX100, & SnCl4 with PEG600 were sprayed onto preheated substrates to deposit thin films of SnO2, SnO2-TX100, & SnO2-PEG600, respectively. A 20 ml solution is spritzed every time. As bases, we used commercially available laboratory glass slides that were 25 mm x 75 mm and 1 mm thick. The slides were cleaned with ethanol, dried, and then placed in a laboratory oven set at around 50˚C before deposition. The substrate's temperature was kept constant at 400˚C utilising a variac & digital temperature controller. The distance between the nozzle and the substrate was maintained at 35 cm. It took approximately 5-6 minutes to spray the entire 20 ml solution. The substrate remains stationary while the nozzle moves back and forth on a line with the help of a programmed stepper motor & micro controller. The programme allows the user to adjust the nozzle's speed & number of cycles to be repeated during the deposition process, ensuring that the solution is applied uniformly. Turning off the heater and letting the SnO2 films cool to room temperature naturally was done once the spray was finished.

CHEMICAL SPRAY PYROLYSIS METHOD

Bhavan Godbole (2009), the Chemical Spray Pyrolysis (CSP) method is widely utilised since it is easy, cheap, & effective. According to P.S. Patil (1999), this approach is useful for producing thin films of the desired thickness that are homogeneous and uniform. The production of nanoparticles also makes use of CSP. Many researchers over the past 20 years have used the CSP method to create various nanoparticles. In their 2004 study, Wei-Ning Wang et al. used the low pressure CSP method to manufacture Ni particles. Nanoparticles were synthesised by Kikuo et al. (2003) using CSP. Several factors influence the films' physical, electrical, or optical properties in this method, including air pressure, substrate temperature, deposition rate, distance between the nozzle & substrate, and cooling rate after deposition [G.Korotcenkov, I.Blinov 2007].

A mechanical arrangement for one-dimensional motion, an air compressor, and a spray nozzle make up the spraying system. The components of a heating unit include a variac, a temperature indicator, a thermocouple& hot plate. By adjusting the current passing through the hotplate, the substrat's temperature could be regulated using a variac. A metal container houses the spray nozzle or hot plate on a glass substrate; an exhaust fan is attached to the container's outlet to remove the harmful gases that are released when the spray solution decomposes. Figure.1 is a schematic of the Chemical Spray Pyrolysis setup, and Figure.2 is an image of the same.

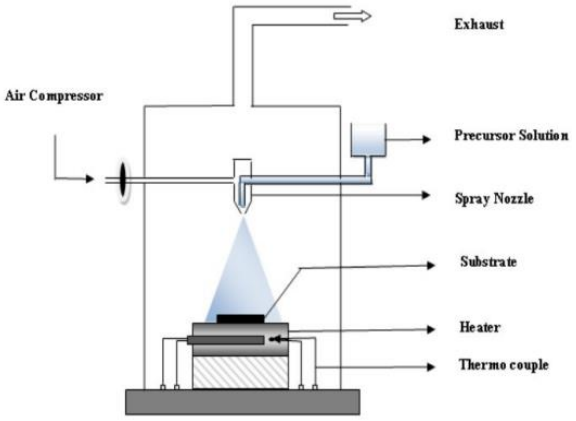

Figure 1: Chemical Spray Pyrolysis Unit Diagram

Figure 2: Homemade Spray Pyrolysis Unit Photo

METAL OXIDE THIN FILM CHARACTERIZATION

Additional characterisation of the prepared SnO2-Surfactant composite films was carried out. The crystal state of these films was studied using an X-ray diffractometer (Ultima IV Japan) equipped with CuKα radiation (λ=1.5405 Å) operating at 40 mA and 40 kV with a scanning rate of 0.02˚ per second. Specord-200 plus, a UV-VIS spectrometer made in Germany, was used to examine the films' optical characteristics between 200 and 1100 nm. The films' surface morphology was examined utilising a scanning electron microscope (EHT8KVm, 100KX WD 5nm, made by ZIESS Optical Systems, Germany). Additionally, the elemental composition was examined by scanning the EDAX spectrum from 0 to 15 keV. The films' current-voltage (I-V) properties were investigated with the use of a Keithley 2636A, a programmed source metre. Using a digital multimeter to measure resistance & digital thermometer with an alomel-chromel thermocouple, we investigated the films' sensing behaviour in terms of resistance fluctuation using our custom-built setups.

XRD Technique

An essential experimental method for studying all factors pertaining to solid crystal structures is X-ray diffraction (XRD). X-ray powder diffraction (XRD) studies of samples reveal crystal structures, which aid in comprehending the structure of bulk materials and, by extension, nanomaterials. References: Y. Waseda (2011) and B.D. Cullity (1978).

X-ray Diffraction according to Bragg's Law

The dispersed rays constructively interfere and powerful reflected rays are created when a parallel beam of X-rays with a wave length corresponding to the interatomic distance & interplanar spacing is encountered at a given grazing angle. As seen in figure 3, visualise a beam of parallel rays AO and BP that hit atoms at O and P, respectively, creating an angle θ with the crystal planes that have Miller indices h, k, & l. The scattered rays are OA1 & PB1. The OP measures how far apart two successive planes are.

The divergence of the AOA1 & BOB1 beams' paths is

$$MP + PN = 2\,(OP)\,\text{Sin}\,\theta = 2d\,\text{Sin}\,\theta$$

They will interfere productively if the path difference is proportional to the integral multiple of μ, the X-ray wave length.

Consequently, 2d Sin θ = n λ, where n = 1, 2, 3...

The aforementioned formula represents Bragg's Law of Diffraction..

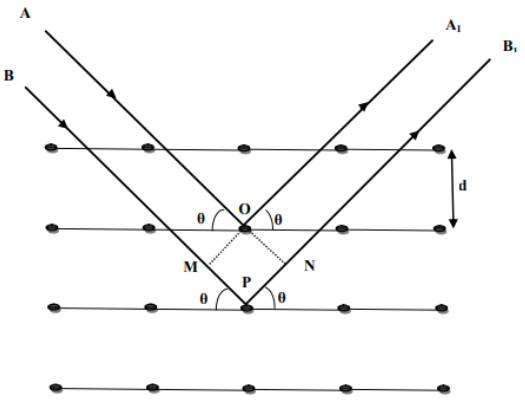

Figure 3: The X-ray beam is reflected from a pair of parallel surfaces.

X-ray Diffratometer

The most popular method for determining the crystal structure of polycrystalline samples, thin films, & nanoparticles is the Powder Diffratometer, also known as the Debye-Scherrer Diffratormeter. A sample holder, an X-ray detector, and a source of monochromatic X-rays are the three main components of an X-ray diffractometer, as shown in figure 4. We can spin the samples & detector on an axis that goes through the middle of the samples & perpendicular to the paper's surface. For this purpose, samples are typically prepared as powders, thin films, etc. The angle 2θ formed by the diffracted rays and the direction of the incident beam is significant. The scattered beam can be collected by positioning the collector. The intensity of scattered X-rays plotted against 2θ (200 to 1600) yields the diffraction pattern utilised for investigation.

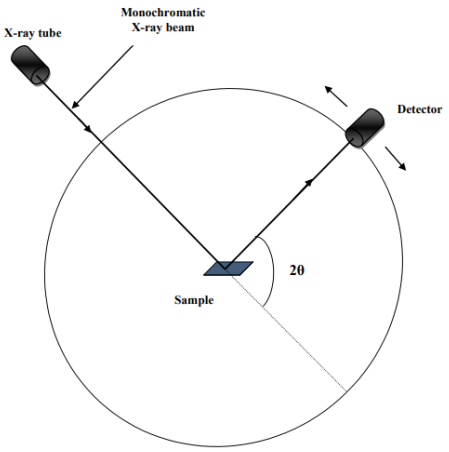

Figure 4: Illustration of an X-ray diffractometer

Debye Scherrer Rule

The X-ray peak broadening is caused by the normally finite size effect of the crystallites. When the size of the crystallite drops below a specific threshold (200 nm), the X-ray beam becomes even more widened. A. Shah (2011) & J.F. Moulder (1995). The Debye-Scherrer formula is used to

determine the grain size from the diffracted beam's broadening.

$$D = \frac{k\lambda}{ß Cos\theta}$$

Wherever,

D - Diameter of the grain,

λ - Wave length of X-rays,

θ - Bragg angle or Diffraction angle,

ß – Full width at half maximum (FWHM) of diffraction peak

k- Scherrer's constant, its value is of the order of 1 for normal crystals (normally k=0.9 is utilized)

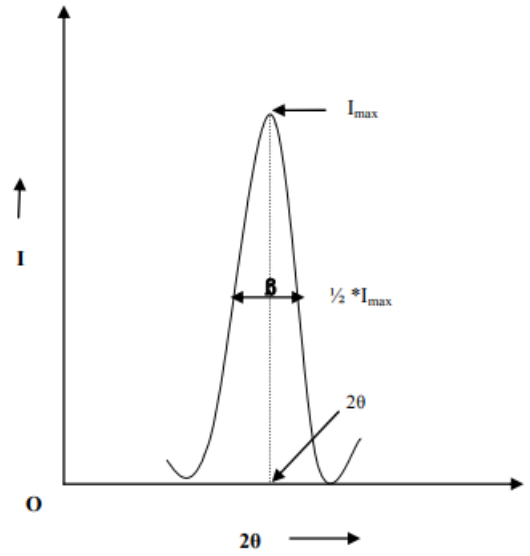

Figure 5: Evaluation of grain size utilising Debye-Scherrer's X-ray peak

SCANNING ELECTRON MICROSCOPE (SEM)

When compared to optical microscopes, electron microscopes are very comparable [Sulabha K. Kulkarni 2009; M.A. Shah 2011]. The detection process in an optical microscope involves the scattering of electromagnetic waves from the specimen [M.A. Hayat 1974]. To direct the light beam onto the specimen, a series of lenses is used. In an electron microscope, the glass lenses are replaced with electrostatic & magnetic ones, and the electron beam is utilised instead of electromagnetic waves. Electrons have the advantage of having their wavelength set to a very small amount by simply adjusting their energies, which allows for higher resolution. Figure 6 shows how the electron microscope is similar to the optical microscope. You can see all the necessary parts in the picture.

Typically, electrons are released from the heated filament in a scanning electron microscope. The cold cathode can occasionally release electrons. A extremely strong electric field is used to cause the cold cathode to emit electrons. Its other name is field emitter. This type of SEM is known as FE-SEM.

Scatter EM allows for the detection of sample-backscattered electrons. Electrostatic or magnetic lenses are employed to concentrate the electron beam into an extremely tiny point. Most frequently employed are electrostatic lenses. A scanner rasters the beam across the sample's surface, & detector gathers the electrons that scatter off the surface. A picture of the sample is created by combining a signal from the electron collector with an amplified signal from the scan generator. Placing the filament & sample in a vacuum chamber (with a vacuum of about 10-5 torr) prevents oxidation & contamination while also reducing the number of collisions between molecules & electrons. Nevertheless, there are environmental microscopes that can function under a high pressure of only a few torrs. Preparation of the sample is not necessary. To keep the pressure differential large, the vacuum system's accelerated electrons enter the sample chamber through a narrow foil or aperture.

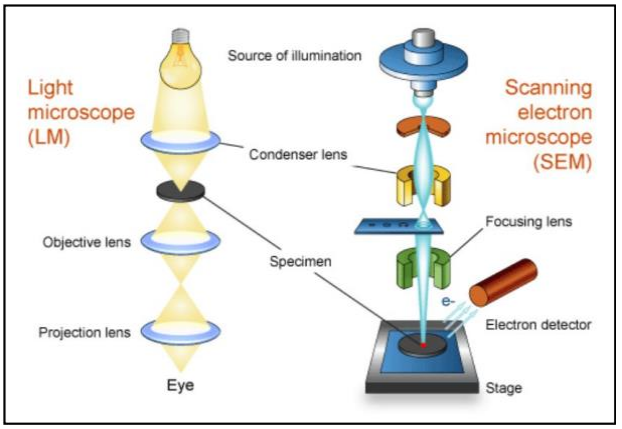

Figure 6: Comparison of Scanning Electron Microscopes with Optical Microscopes

ENERGY DISPERSIVE ANALYSIS OF X-RAY (EDAX)

With a scanning electron microscope, this technique can be applied to determine the sample's material composition [Sulabha K. Kulkarni 2009; M.A. Shah 2011]. In a SEM, X-rays emitted by an electron with a high energy that hits a sample are unique to that atom. By comparing the intensity of these distinctive X-rays, one can deduce the sample's makeup.

UV-Vis Spectrometer

In bulk, colloidal, thin film, & nanostructure forms, optical absorption spectroscopy is a tool for studying insulators, metals, and semiconductors. The optical energy gap is present in semiconductors & small

number of insulators. [M.A. Shah 2011; Sulabha K. Kulkarni 2009]. Absorption does not occur when the energy of the incoming photons is not high enough to transfer electrons from the valence to the conduction band. A sharp increase in absorption happens when the photon energy is adequate to excite the electrons from the valence band to the conduction band minimum. Absorption of photons with energies greater than this critical value persists.

To comprehend electronic structure & transitions between the conduction and valence bands, one can examine the absorbed or reflected intensity as a function of wave length from ultraviolet to infrared. The absorption edge can move when the particle size of a substance decreases. The shift that is typically discernible at shorter wave lengths is called the blue shift.

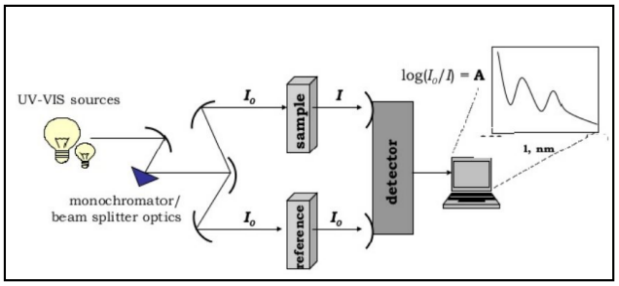

Figure 7: UV-Vis spectrometer schematic.

It produces radiation in the visible & ultraviolet (UV/VIS) ranges using high-intensity lamps placed in separate spectral regions. The sample is exposed to certain wavelengths by means of a monochromator, which is typically a grating or prism. The sample transmits most wavelengths while absorbing or reflecting some, depending on its characteristics. A photo detector sends data to a computer or recorder based on the transmitted or absorbed intensity at various wavelengths. The radiation beam is divided in half at the source, with half of it passing through all the components that are the same except for the sample. To determine the signal only caused by the sample, the reference signal & sample signal are compared.

Figure 8: Photograph of UV – Vis Spectrometer

MEASUREMENTS OF CURRENT-VOLTAGE

The Keithley 2400 programmable source metre was connected to a computer with a GPIB data card & Lab View programme in order to investigate the current-voltage characteristics. A two-probe conductivity setup was used to characterise all of the samples. To determine the films' resistance, a two-probe setup is employed. The change in resistance can be measured by directly connecting the source metre to the sensor units.

Figure 9: Keithley Computer-Interfaced Source Metre Photograph

CONCLUSION

A sensor is an instrument that can take in signals from the physical, chemical, or biological world & transform them into an electrical signal that may be used in electronic circuits. This interpretation might be bolstered by looking at the word sensor's etymological roots. When the gas concentration in the air changes, the sensing element's chemical characteristics shift accordingly. The transducer converts the chemical signal to an electrical signal that may be easily measured. It is possible to detect this reaction through measuring changes in capacitance, work function, mass, optical characteristics, or the reaction energy produced by the gas/solid interaction, additionally to the conductivity change of the gas-sensing material.

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